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(54) Method for curing ultraviolet-curable silicone compositions

(57) There is disclosed herein a method for curing UV-curable silicone compositions, characterized by the formation of cured silicone, having a low-tack surface that is harder than the interior. The cured silicone is pro-

duced by exposing an UV-curable silicone composition to ultraviolet radiation at a ratio of the exposure dose for wavelengths of 200 to 280 nm (excluding 280 nm) to the exposure dose for wavelengths of 280 to 400 nm of 0.5 to 10.0.

1

EP 0 728 799 A1

2

Description

The present invention provides to a method for curing ultraviolet (UV) curable silicone rubber compositions that yield, upon exposure to a particular type of UV radiation, cured silicone having a low-tack surface which is harder than the interior.

UV-curable silicone compositions, which cure rapidly into silicone under UV illumination, are widely used in industrial applications. These compositions are exemplified by JP-A 57-52371; EP 0400785; and U.S. Patent 4,707,503. The irradiation of these silicone compositions with ultraviolet light is carried out using well-known light sources, such as mercury lamps, hydrogen discharge tubes, xenon discharge tubes, metal halide lamps, and so forth.

However, the direct exposure of UV-curable silicone compositions to UV light from these light sources also yields cured silicone with a very tacky surface. This can cause difficult handling. In addition, such surfaces readily pick up dirt and dust, which causes a substantial deterioration in appearance. These problems are particularly acute with lower-hardness cured silicones. For example, when a silicone gel is formed on the surface of an optical semiconductor element using a UV-curable silicone composition, the dust and dirt picked up by the surface will cause a major decline in the performance of the element.

We have performed extensive investigations to solve the above-described problem. As a result, we found that UV light in the short wavelength region is a major contributor to curing silicone compositions at the surface. We also found that low surface tack cured silicone, whose surface is harder than its interior, is also produced by exposure to UV light at a short wavelength exposure to long wavelength exposure dose ratio within a particular range. Our invention was achieved based on these discoveries.

In specific terms, then, the present invention takes as its object the introduction of a method for curing UV-curable silicone compositions that characteristically produce cured silicone rubbers having a low-tack surface, which is harder than the interior. These rubbers are attained by exposing a UV-curable silicone composition to a particular type of UV radiation.

The method of the present invention is specifically characterized by the formation of cured silicone by exposure of an UV-curable silicone composition to ultraviolet radiation at a ratio of the exposure dose for wavelengths of 200 to 250 nm (excluding 230 nm) to the exposure dose for wavelengths of 280 to 400 nm of 0.5 to 10.0.

The nature of the UV-curable silicone composition subjected to the present invention is not crucial. Typical silicone compositions that may be used include, those in which the base ingredient is acrylamido-functional organopolysiloxane, as in JP-A 57-52371 or EP 0400785; and those in which the base ingredients are an organo-

polysiloxane with at least 2 mercaptoalkyl groups in each molecule and an organopolysiloxane with at least 2 alkanyl groups in each molecule, as in U.S. Patent 4,707,503. Other operable UV-curable silicone compositions are those in which the base ingredient is an alkanyl-functional organopolysiloxane; those in which the base ingredient is an acrylic-functional or methacrylic-functional organopolysiloxane; and those in which the base ingredients are an organopolysiloxane having at least 2 alkanyl groups in each molecule and an organopolysiloxane having at least 2 silicon-bonded hydrogen atoms in each molecule. Preferred for the present invention are UV-curable silicone compositions of the aforementioned patents.

The nature of the acrylamido-functional organopolysiloxane is not crucial, and it is exemplified by, but is not limited to: dimethylpolysiloxane, endblocked by acrylamidopropyldimethylsiloxy at one or both molecular terminals; dimethylpolysiloxane, endblocked by N-methylacrylamidopropyldimethylsiloxy at one or both molecular terminals; dimethylpolysiloxane, endblocked by acrylamidoisobutylidimethylsiloxy at one or both molecular terminals; dimethylpolysiloxane, endblocked by N-methylacrylamidobutylidimethylsiloxy at one or both molecular terminals; dimethylpolysiloxane-methylphenylsiloxane copolymer, endblocked by acrylamidopropylmethylsiloxy at one or both molecular terminals; dimethylsiloxane-methylphenylsiloxane copolymer, endblocked by N-methylacrylamidobutylidimethylsiloxy at one or both molecular terminals; dimethylsiloxane-methylphenylsiloxane copolymer, endblocked by acrylamidoisobutylidimethylsiloxy at one or both molecular terminals; dimethylsiloxane-diphenylsiloxane copolymer endblocked by acrylamidopropylmethylsiloxy at one or both molecular terminals; dimethylsiloxane-diphenylsiloxane copolymer endblocked by acrylamidobutylidimethylsiloxy at one or both molecular terminals; dimethylsiloxane-methylphenylsiloxane copolymer endblocked by acrylamidopropylmethylsiloxy at one or both molecular terminals; dimethylsiloxane-methylphenylsiloxane copolymer endblocked by acrylamidobutylidimethylsiloxy at one or both molecular terminals; diphenylsiloxane-methylphenylsiloxane copolymer endblocked by acrylamidopropyldiphenylsiloxy at one or both molecular terminals; methylphenylpolysiloxane endblocked by acrylamidopropylmethylphenylsiloxy at one or both molecular terminals; diphenylpolysiloxane endblocked by acrylamidopropyldiphenylsiloxy at one or both molecular terminals; methylphenylpolysiloxane, endblocked by acrylamidopropyldiphenylsiloxy at only one molecular chain terminal; dimethylpolysiloxane bearing acrylamidopropyl in a nonterminal position; dimethylpolysiloxane bearing N-methylacrylamidopropyl in a nonterminal position; dimethylpolysiloxane bearing acrylamidoisobutyl in a nonterminal po-

sition; dimethylpolysiloxane bearing N-methylacrylamidoisobutyl in a nonterminal position; dimethylsiloxane-methylphenylsiloxane copolymer bearing acrylamido-propyl in a nonterminal position; dimethylsiloxane-methylphenylsiloxane copolymer bearing acrylamidoisobutyl in a nonterminal position; dimethylsiloxane-methylvinylsiloxane copolymer bearing acrylamidopropyl in a nonterminal position; and dimethylsiloxane-methylvinylsiloxane copolymer bearing acrylamidoisobutyl in a nonterminal position. The aforesaid organopolysiloxanes may be used singly or as mixtures of two or more selections.

The nature of the mercaptoalkyl-functional organopolysiloxane is also not crucial, and it is exemplified by, but is not limited to: dimethyl(3-mercaptopropyl)siloxane-endblocked dimethylpolysiloxane; dimethyl(3-mercaptopropyl)siloxane-endblocked dimethylsiloxane-methylphenylsiloxane copolymer; dimethyl(3-mercaptopropyl)siloxane-dimethylsiloxane copolymer; methyl(3-mercaptopropyl)siloxane-dimethylsiloxane-methylphenylsiloxane copolymer; methyl(3-mercaptopropyl)siloxane-diphenylsiloxane copolymer; 3-mercaptopropyl(phenoxy)siloxane-dimethylsiloxane copolymer, and 3-mercaptopropyl(phenyl)siloxane-diphenylsiloxane copolymer. These mercaptoalkyl-functional organopolysiloxanes may also be used singly or as mixtures of two or more selections.

The alkenyl-functional organopolysiloxane is exemplified by, but is not limited to: dimethylvinylsiloxy-end-blocked dimethylpolysiloxane; dimethylvinylsiloxy-end-blocked dimethylsiloxane-methylphenylsiloxane copolymer; dimethylvinylsiloxy-end-blocked dimethylsiloxane-diphenylsiloxane copolymer; dimethylvinylsiloxy-end-blocked dimethylsiloxane-methylvinylsiloxane copolymer; dimethylvinylsiloxy-end-blocked dimethylsiloxane-phenylvinylsiloxane copolymer; dimethylvinylsiloxy-end-blocked dimethylvinylpolysiloxane, methylvinylsiloxane-dimethylsiloxane copolymer; methylvinylsiloxane-methylphenylsiloxane copolymer; methylvinylsiloxane-diphenylsiloxane copolymer; phenylvinylsiloxane-dimethylsiloxane copolymer; and phenylvinylsiloxane-diphenylsiloxane copolymer. These alkenyl-functional organopolysiloxanes may also be used singly or as mixtures of two or more selections.

While the amount of alkenyl-functional organopolysiloxane is not crucial, it is preferably added in a quantity that will give 0.1 to 5.0 moles of alkenyl radical from this organopolysiloxane per mole of mercaptoalkyl radical in the mercaptoalkyl-functional organopolysiloxane.

Insofar as the object of the invention is not impaired, our UV-curable silicone compositions may also contain a photoinitiator as an optional component. The photoinitiators that may be used are acetophenone and its derivatives, such as dichloracetophenone, trichloroacetophenone, tert-butyltrichloroacetophenone, 2,2-diethoxyacetophenone, and p-dimethylaminooacetophenone; benzoin and its derivatives, such as benzoin me-

thyl ether, benzoin ethyl ether, benzoin butyl ether, and benzoin n-butyl ether; benzophenone and its derivatives, such as 2-chlorobenzophenone, p,p'-dichlorobenzophenone, and p,p'-bisdiethylaminobenzophenone; p-dimethylaminopropiophenone; Michler's ketone; benzyl; benzyl dimethyl ketal; monosulfido; thioxanthone; 2-chlorothioxanthone; 2-methylthioxanthone; azoisobutyronitrile; benzoin peroxide; di-tert-butyl peroxide; 1-hydroxycyclohexyl phenyl ketone; 2-hydroxy-2-methyl-1-phenylpropan-1-one; 1-(4-isopropylphenyl)-2-hydroxy-2-methylpropan-1-one; methyl benzoylformate; diphenyl sulfide; anthracene; 1-chloranthraquinone; diphenyl disulfide; diacetyl; hexachlorobutadiene; pentachlorobutadiene; octachlorobutadiene; and 1-chloromethylnaphthalene. Particularly preferred photoinitiators are acetophenone, benzoin, benzophenone, and their derivatives. The quantity of photoinitiator that may be used in the present invention is not critical. However, the preferred quantity of photoinitiator is 0.1 to 10 weight percent based on the total composition.

Our UV-curable silicone composition may contain, for example, the following as optional components, again insofar as the object of the invention is not impaired: photosensitizers, including n-butylamine, di-n-butylamine, tri-n-butylphosphine, allylthiourea, S-benzylisothiuronium p-toluenesulfonate, triethylamine, and diethylaminoethyl methacrylate; inorganic fillers, turned silica and quartz powder, thermally conductive fillers, including electrically conductive fillers, metals and including metal compounds; pigments; dyes; and organic solvents, such as hexane, heptane, toluene, and xylene.

The form of the cured silicone afforded by our curing method is not crucial, and the cured silicone may be, for example, a gel, rubber, or resin. Gels are preferred because they fully exploit the effects of the present invention. The viscosity of our UV-curable silicone composition is not crucial, but a viscosity at 25°C from 10 to 100,000 mPa.s (centipoise) is preferred for good handling characteristics of the composition and good physical properties in the cured silicone product.

Our curing method requires that the UV-curable silicone composition be illuminated with ultraviolet light at a ratio of the exposure dose for wavelengths of 200 to 280 nm (excluding 280 nm) to the exposure dose for wavelengths of 280 to 400 nm (hereinafter the short-wavelength to long-wavelength exposure dose ratio or SWED/LWED ratio) of 0.5 to 10.0. The surface of the cured silicone will be extremely tacky when curing is effected by direct illumination with UV light from known sources (e.g., mercury lamps, hydrogen-discharge tubes, xenon-discharge tubes, and metal halide lamps) with their SWED/LWED ratios below 0.5. At the other end of the range, when UV light is used at a SWED/LWED ratio in excess of 10.0, the resulting cured silicone will have a very hard surface with a large number of cracks in its surface. No particular restrictions apply to the specific technique used in our curing method to effect exposure to UV light at a SWED/LWED ratio of

0.5 to 10.0. For example, a UV-cut filter can be used with a conventional light source having a SWED/LWED ratio below 0.5 to adjust the SWED/LWED ratio to 0.5 to 10.0.

With regard to the use of conventional light sources in our curing method, UV-cut filters are available commercially for adjusting the SWED/LWED ratio of said conventional light sources to 0.5 to 10.0. Stacks of these filters may also be used. Alternatively, direct exposure to UV light from a conventional source may be used, while at the same time effecting exposure to UV light from a conventional source that has been passed through a UV-cut filter. As another alternative, these two types of exposure can be carried out sequentially rather than simultaneously. The exposure dose at 280 to 400 nm and the exposure dose at 200 to 280 (excluding 280 nm) irradiated on the UV-curable silicone composition can be readily determined using an ultraviolet dose meter or similar device.

The conditions under which our UV-curable silicone composition is exposed to UV light are not critical for our curing method. For example, the composition can be irradiated in the air, under a vacuum, or in an inert gas (e.g., nitrogen, argon, and helium) at room temperature, while cooling, or while heating to 50°C to 150°C. Irradiation in air at room temperature is particularly preferred.

Our curing method produces cured silicone whose surface is harder than its interior. More particularly, this method produces silicone gel having a tack-free silicone rubber skin at its surface. As a result of these features, this curing method is useful for the formation of protective coatings on the surface of semiconductor elements; for the formation of conformal coatings on the surface of electronic circuit substrates; for the formation of print patterns; and the like. Our curing method is especially useful for the surface formation on semiconductor elements of silicone gel which presents a tack-free silicone rubber skin that is resistant to the adhesion of dirt and dust.

The method according to the present invention for curing UV-curable silicone compositions will be explained in greater detail through working examples. The viscosity values reported in the examples were measured at 25°C. To evaluate the status of the cure at the surface and in the interior of the cured silicone, the UV-curable silicone composition was cast on an aluminum dish to a thickness of approximately 5 mm. After exposure to UV light, the cured silicone was removed from the aluminum dish, and both the surface and the interior of the cured silicone were inspected by touch.

Example 1

A UV-curable silicone composition was prepared by mixing 2 weight parts of 2-hydroxy-2-methyl-1-phenylpropan-1-one to homogeneity into 100 weight parts of dimethylsiloxane-methylphenylsiloxane copolymer, endblocked at one molecular terminal with N-methylacry-

ylamidebutyldimethylsiloxy and endblocked at the other terminal with trimethylsiloxy. The viscosity, at 25 °C, of the copolymer was 3000 mPa.s (centipoise). The molar ratio of dimethylsiloxane to methylphenylsiloxane in the copolymer was 10:1.

This composition was directly irradiated with UV light from a high-pressure mercury lamp while being simultaneously irradiated with UV light from a high-pressure mercury lamp that had been passed through a UV-cut filter. The product was a silicone gel having a low-tack silicone rubber skin at the surface. This silicone gel was produced using an exposure dose of 3 J/cm² for the 280 to 400 nm wavelengths and an exposure dose of 4.8 J/cm² for the 200 to 280 nm wavelengths (excluding 280 nm).

Example 2

The following were mixed to homogeneity to give a UV-curable silicone composition: 8 weight parts of trimethylsiloxy-endblocked dimethylsiloxane-3-mercaptopropyl(methyl)siloxane copolymer [viscosity = 100 mPa.s (centipoise), mercapto group content = 4.0 weight%], 100 weight parts of dimethylvinylsiloxy-end-blocked dimethylpolysiloxane [viscosity = 2,000 mPa.s (centipoise), vinyl content = 0.23 weight%], and 1 weight part of 1-(4-isopropylphenyl)-2-hydroxy-2-methylpropan-1-one.

This UV-curable silicone composition was directly irradiated with UV light from a high-pressure mercury lamp while being simultaneously irradiated with UV light from a high-pressure mercury lamp that had been passed through a UV-cut filter. The product was a silicone gel having a low-tack silicone rubber skin at the surface. This silicone gel was produced using an exposure dose of 0.5 J/cm² for the 280 to 400 nm wavelengths and an exposure dose of 0.8 J/cm² for the 200 to 280 nm wavelength (excluding 280 nm).

Comparative Example 1

Direct exposure of the UV-curable silicone composition prepared in Example 1 with UV light from a high-pressure mercury lamp produced a silicone gel having a very tacky and soft silicone rubber skin at its surface. This silicone gel was produced using an exposure dose of 3 J/cm² for the 280 to 400 nm wavelengths and an exposure dose of 1.2 J/cm² for the 200 to 280 nm wavelengths (excluding 280 nm).

Comparative Example 2

The UV-curable silicone composition prepared in Example 1 was directly irradiated with UV light from a high-pressure mercury lamp and thereafter irradiated with UV light from a high-pressure mercury lamp that had been passed through a UV-cut filter. The product was a silicone gel having a hard silicone resin skin at

the surface. This silicone gel was produced using an exposure dose of 3 J/cm² for the 280 to 400 nm wavelengths and an exposure dose of 40 J/cm² for the 200 to 280 nm wavelengths (excluding 280 nm). Numerous cracks were also observed in the silicone resin skin. 5

Comparative Example 3

Direct exposure of the UV-curable silicone composition prepared in Example 2 with UV light from a high-pressure mercury lamp produced a silicone gel having a very tacky and soft silicone rubber skin at its surface. This silicone gel was produced using an exposure dose of 0.5 J/cm² for the 280 to 400 nm wavelengths and an exposure dose of 0.2 J/cm² for the 200 to 280 nm wavelengths (excluding 280 nm).

The method according to the present invention for curing UV-curable silicone compositions characteristically comprises exposing a UV-curable silicone composition to ultraviolet light at a ratio of the exposure dose for wavelengths of 200 to 280 nm (excluding 280 nm) to the exposure dose for wavelengths of 280 to 400 nm of 0.5 to 10.0. As a result, our method can produce a low surface tack cured silicone whose surface is harder than its interior.

Claims

1. A method for curing UV-curable silicone compositions, comprising the step of exposing an UV-curable silicone composition to ultraviolet radiation having an exposure dose ratio of 0.5 to 10.0, wherein the exposure dose ratio is the exposure dose for the wavelengths from 200 nm up to, but not including 280 nm, divided by the exposure dose for the wavelengths from 280 nm to 400 nm. 30
2. The method of claim 1, wherein the UV-curable silicone composition yields, upon cure, a silicone gel having a silicone rubber covering at its surface. 40
3. The method of claim 1, wherein the UV-curable silicone composition comprises an acrylamide-functional organopolysiloxane. 45
4. The method of claim 1, wherein the UV-curable silicone composition comprises A) an organopolysiloxane having at least 2 mercaptoalkyl groups in each molecule, and B) an organopolysiloxane having at least 2 alkenyl groups in each molecule, in a quantity that provides 0.1 to 5 moles of alkenyl group per mole of mercaptoalkyl group. 50

EP 0 728 799 A1

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EUROPEAN SEARCH REPORT

Application Number
EP 96 30 1095

DOCUMENTS CONSIDERED TO BE RELEVANT			CLASSIFICATION OF THE APPLICATION (INCLUDE)						
Category	Citation of documents who indication, where appropriate, of relevant passages	Relevant to claim							
A	EP-A-0 204 427 (RAYCEHM CORPORATION) 18 December 1986 * claims 6,18 *	1	C08J3/28 //C08L83:04						
A	EP-A-0 550 239 (DOW CORNING CORP.) 7 July 1993 * claims 1,3,4 *	1							
A	DATABASE WPI Derwent Publications Ltd., London, GB; AN 92-189820[23] XP002003775 & JP-A-04 126 730 (MITSUBISHI RAYON CO. LTD.) . 27 April 1992 * abstract *	1							
P,X	DATABASE WPI Derwent Publications Ltd., London, GB; AN 95-144871[19] XP002003273 & JP-A-07 078 219 (DAINIPPON INK & CHEM. INC.) , 14 March 1995 * abstract *	1							
			TECHNICAL FIELDS SEARCHED (INCLUDE)						
			C08J C08L C08F						
<p>The present search report has been drawn up for all claims</p> <table border="1"> <tr> <td>Date of search</td> <td>Date of compilation of the search</td> <td>Examiner</td> </tr> <tr> <td>THE HAGUE</td> <td>23 May 1996</td> <td>Niaounakis, M</td> </tr> </table> <p>CATEGORY OF CITED DOCUMENTS</p> <p>X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background C : non-patent disclosure P : intermediate document</p> <p>T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons R : member of the same patent family, corresponding document</p>				Date of search	Date of compilation of the search	Examiner	THE HAGUE	23 May 1996	Niaounakis, M
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THE HAGUE	23 May 1996	Niaounakis, M							